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New Methods for Trending Varnish Buildup in Mineral Turbine Oils

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Abstract

The topic of varnish in Turbine Oils is a very popular topic today. The changes in Gas Turbine designs over the last decade, coupled with the changes in turbine oil formulations, have led to a real and identifiable problem of oil-related turbine trips that are caused by an oxidation by-product called varnish. This has resulted in changes in turbine oil asset-management, changes in turbine oil filtration methods, and shortened turbine oil intervals, especially with gas turbines that have sensitive servo-valve controls with micro orifices. In addition to changing the patterns in how turbine oil is managed, this contamination has created challenges to the oil testing industry to come up with a method for varnish that is reliable, rapid, and low in analysis costs. In a previous paper [1], the authors have documented results that show the direct correlation between a simple Varnish-Testing procedure called Varnish Potential Index (VPI, a proprietary test), and the Linear Sweep Voltammetry test (RULER® as per ASTM D-6971 [2,3]). The correlation is known to have an inverse relationship, as the oil degrades in-service, and the remaining Antioxidant Additive percentage (Remaining Useful Life or RUL%) is reduced, the Varnish Potential Index goes up, reflecting the increasing Varnish buildup.

To further establish the direct correlation between the two test methods, the authors decided to challenge the relationship in the reverse mode; in other words, if a degraded turbine oil could be cleaned or purified by its varnish buildup in-service use, would the oil testing results then show a reduction in VPI, an improvement in antioxidant strength, and improvements in other ASTM tests, thus further validating the direct relationship between varnish buildup and antioxidant depletion?

Introduction

It is generally recognized that a majority of the contamination in mineral-based turbine lubricating oils and hydraulic lubricating oils consists of soft-contaminants that are not measurable by conventional particle counting technology or methods. This is generally thought to be due to the gel nature of the contaminants (they are neither liquid nor solid in state) and due to the extremely small size of these contaminants (usually less than 1 micron in size). The contaminants that are of a resinous, sticky nature and that are yellow in color have often been referred to as "varnish," for lack of a better term. These varnish contaminants are usually found to have adiabatic compression or electro static discharge as their root causes. Other oxidation by-products from additive depletion and oxidative degradation are sometimes called sludge, and may also be measured by this method, although it should be noted that varnish and sludge may exist separately from each other, or exist in conjunction with each other, and both types of contaminants need to be understood and recognized.

Several attempts have been made to develop a test method for varnish in mineral turbine oils. These methods have usually been centered on dilution of the oil with a solvent, followed by strong vacuum filtration of the oil/solvent mixture, through a membrane patch. Various ideas have been proposed on how to quantify the varnish contaminant deposited on the membrane patch, either by membrane patch weight or membrane patch color. Most of these methods work well in the later, more excessive stages of the contamination process, when the problem has become severe in nature and the oil has reached a critical saturation point of these contaminants. However, a major drawback with these testing methods is that they tend to exhibit a low-slope data increase in the early stages, which does not lend itself well to trending analysis and prediction. Because of this problem, a more sensitive test was desired, one that was able to better monitor the early stages of increases in these varnish contaminants, to give data with better resolution, and to be able to better predict the timing and severity of the contamination.

In an effort to be able to better predict this timing and severity, it was recognized that varnish, as a gel substance, is very fragile. And as a fragile contaminant, it may be easier to quantify its existence and presence if it were treated with more care and caution. This was certainly not the case by dilution with a highly solvent liquid and then an aggressive vacuum-filtration. It was thought that much of the varnish data had been minimized and disturbed (lost) by this aggressive treatment. It was noted in the work by Sasaki et al [4], that varnish was easy to detect by simple scanner technology and colorimetric analysis in the RGB or other color scales. However, their work was done in the dilute-and-vacuum-filter style, and only yielded results with good resolution in the severe contaminant concentrations. A new approach was the idea to stain the oil on a white cellulose nitrate membrane, and then use colorimetric analysis for trending purposes. The staining process allows the unadulterated oil to slowly absorb into the capillaries of the membrane, and not be removed from the measured media, and certainly to experience fewer disturbances as to the liquid/solid state issue. This method has been found to give excellent results in the early stages of an oil's life, from initial service well into the later problem stages. And it has been found to correlate well with other conventional testing methods, such as Linear Sweep Voltammetry (RULER®), Acid Number (AN) and Viscosity increases, FTIR analysis, Gravimetric Patch and RPVOT [1].

The Colorimetric Analysis result of the stain was assigned to an Index Scale [4] and is called Varnish Potential Index (VPI) [5]. When VPI values reach the middle to upper end of the index scale (greater than 125 VPI to 255 VPI), it is recommended to combine this testing with Gravimetric Patch Testing for residue weight and visual examination of the Gravimetric patch residue for other indications of

the nature and severity of the varnish and other sludge that may be developing. This test method does not purport to be able to measure varnish tendencies in any other oils than mineral-based turbine lubricating oils and hydraulic lubricating oils. This test is only applicable to oils with natural coloring and is not applicable to oils that have been dyed for identification or other purposes.

VPI Test Method Overview

Stain Preparation

1. Select a new cellulose nitrate membrane write the sample number on the membrane.
2. Place the membrane on the Drying Grill so that the membrane center is not touching any grill rods yet the membrane is supported by the rods at the outer edge of the membrane.
3. Sufficiently agitate the sample and withdraw and dispense 25 microliters of oil on to the center of the membrane.
4. Cover the membranes and record the time of Stain Preparation.

Stain Color Measurement

1. Allow the Stain to dry for a minimum of 12 hours but do not exceed a maximum of 24 hours before measuring the Color of the Stain.
2. Using a PC equipped with suitable photo image retouching software and capable of scanner control, scan the Stain to create an image of the stain with a minimum resolution of 600 dpi (2400 dpi is recommended). Scanners and PC settings should be set to allow for true color imaging, contrast and brightness. Automatic adjustment is allowed for true color balances, but no enhancements should be used. PC monitors should be calibrated by the imaging software or other means for true color.
3. After the Stain image has been scanned and saved, retrieve the image in the photo retouching software and open the image.
4. Using an appropriate color selecting tool from the photo retouching software, measure the RGB Color of the image in the center of the Stain, taking care to measure in an area of obvious average oil staining. Avoid any white spots or dark spots that may appear. Make sure the color selecting tool is set to an average selecting area of at least 5x5 pixels, and is not set to select an individual pixel color. There should be three Color Measurement Values available for recording, one each for Red / Green / Blue. The minimum value for each Color is 0 and the maximum Value for each Color is 255. Record the values for later calculation.

VPI Calculation

1. Calculate the Red-Green (R-G), the Green-Blue (G-B) and the Red-Blue (R-B) as three different Color Differentials.
2. The VPI is defined as the Maximum Color Differential, which should always be the Red-Blue (R-B) Value.

VPI = (R-B)

If the R-B is not the Maximum Value out of all three values, the test is null and void and the value disregarded.



Figure 1. VPI Patches with Stains in Drying Process Validation Scope

Validation Scope

After initial study of the correlation relationship between the VPI test and other test methods, it was decided to evaluate the VPI test method in the reverse process, in other words, given that VPI shows a good correlation with other oil tests as the oil condition becomes progressively worse, would the same good correlation relationship exist between VPI and the other test methods as the oil condition was in a constantly improving condition such as when an oil was being purified by high-technology means?

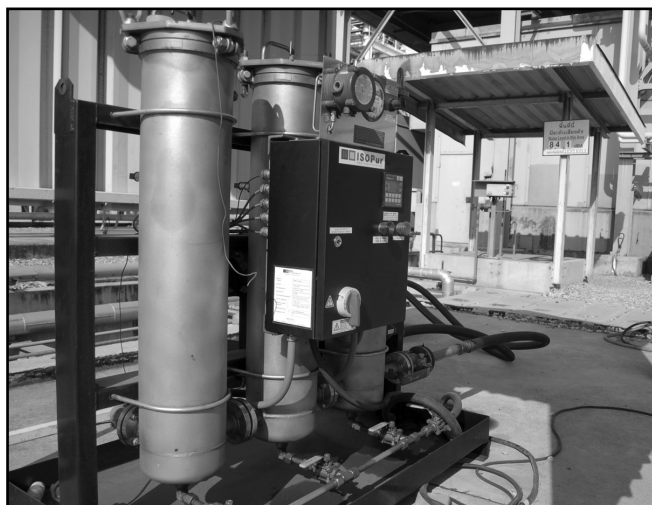


Figure 2. ISOPur HR Filtration Unit in Service

To investigate this question, the test scope was to evaluate two different oils from an SPP (small cogeneration power plant) in Thailand. The lubricating oils of both the gas turbines and steam turbine were to be purified with an ISO-Pur Balanced Charge Agglomeration (BCA) electrostatic purification system, and monitored with VPI testing and other conventional testing methods. The BCA process, patented by ISOPur Fluid Technologies Inc.[6], introduces a controlled current into the fluid media, which charges the contaminated particles producing enhanced positive and negative charged particles. These charged particles are then mixed

within the charging/mixing vessel. During this mixing, the oppositely charged particles combine to form larger particles which are then captured in the proprietary collection element. The agglomerated particles then pass through the fluid system combining with other contaminants which are removed during the subsequent passes through the unit. In this manner, the Fluid Purification System not only cleans the contaminated fluid but after numerous passes through the fluid path, it also cleans the reservoir, piping, and all associated elements of that system.

One of the prime tests to be correlated with VPI was the Linear Sweep Voltammetry (LSV) test, or commercially available as RULER® Technology [2,3,7]. Using voltammetric techniques, the RULER® applies a controlled voltage through an electrode inserted into a prepared sample[8]. As the potential increases the antioxidants become chemically active causing current to increase producing an oxidation wave. In this method, the voltage range of the oxidation wave is related to the identity of the antioxidant, and the peak value indicates the concentration of the antioxidant. The peak value of the oxidation wave is directly related to the concentration of the antioxidants in the sample. The test results are displayed on the computer screen when the test is completed. The oxidation wave produced is viewed and the values are presented in RULER® Numbers, which can be used to track antioxidant depletion rates. RULER® Numbers decrease as antioxidants are depleted thus it is possible to track depletion from test to test as degradation occurs. The instrument compares the RULER® Number of a used oil sample with that of a fresh oil sample (Standard) of the same formulation to determine the percentage of the Remaining Useful Life of the used oil (see also Figure 3).

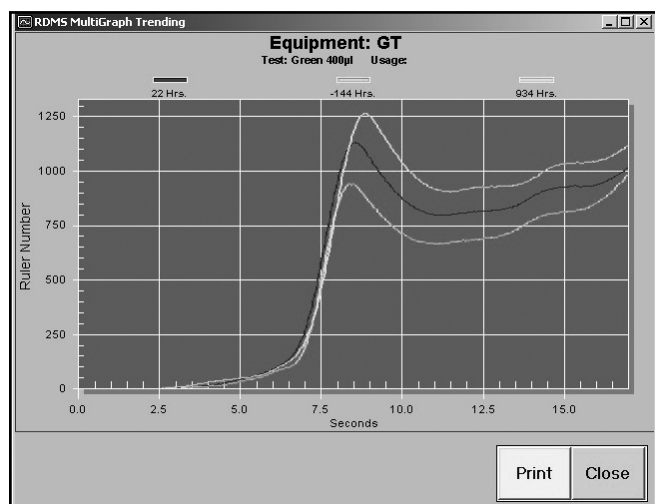


Figure 3. Ruler Multigraph Results for the Gas Turbine Oil Samples

The rationale for choosing RULER® as the Primary correlation test, over the more traditional RPVOT test, is the issue of lack of applicability of RPVOT testing to all types of oils. Of the two types of oils to be tested, the steam turbine oil and the gas turbine oil, both oils were not well suited for RPVOT testing. The steam turbine oil, with a new oil RPVOT value of less than 1,000 minutes, was well

suiting for accurate and repeatable RPVOT testing, while the gas turbine oil has a published new oil RPVOT value of >3,000 minutes, and was known to have accuracy and reproducibility problems when tested by the RPVOT method. Thus RPVOT testing could not be considered a primary test for correlation on the gas turbine oil, but was included in the steam turbine oil correlations. The tests used for correlation with VPI were:

- Linear Sweep Voltammetry or RULER® (% Remaining Useful Life for Remaining Anti-Oxidant Additive)
- Gravimetric Patch weight (mg per 100 ml)
- FTIR Oxidation (abs units at 1800-1670 wave number)
- Particle Count ISO 4406:99 (the # of particles > 4 microns)
- RPVOT {steam turbine only} (in minutes)
- Oil Temperature {gas turbine only} (deg C at the filtration unit)

Steam Turbine Results

The steam turbine was an Alstom Model TC 554 used in a cogeneration situation, with a lubricating oil reservoir holding 6,000 liters of ISO VG 46 oil. The lube oil had accumulated approximately 47,000 running hours prior to the ISO-Pur BCA, Model HR Series, being installed. One of the objectives of purification of the oil was to prevent an oil change at an upcoming scheduled outage of the steam

Sequence #	1	2	3	4	5
Date of Sample	29-08-06	30-08-06	1/9/2006	4/9/2006	5/9/2006
Hours of Filtration	-624	1	47	117	147
Sample #	61522	62794	62818	62975	63042
Varnish Potential Index	113	118	114	101	101
Gravimetric Patch wt mg/100ml	7	6	6	5	4
FTIR Oxidation absorbance units	5.9	5.76	5.68	5.64	5.66
Particle Count # of particles >4µ	573	927	344	411	229
Ruler % Remaining additive	74.2	71.2	74.8	73.4	75.1
RPVOT	128				
Sequence #	6	7	8	9	10
Date of Sample	6/9/2006	7/9/2006	8/9/2006	11/9/2006	12/9/2006
Hours of Filtration	170	195	219	290	311
Sample #	63082	63188	63236	63313	63320
Varnish Potential Index	89	92	93	100	95
Gravimetric Patch wt mg/100ml	4	3	5	5	4
FTIR Oxidation absorbance units	5.63	5.7	5.64	5.62	5.66
Particle Count # of particles >4µ	296	429	468	242	296
Ruler % Remaining additive	81.9	79.9	80.1	83.4	85.6
RPVOT					
Sequence #	11	12	13	14	15
Date of Sample	13-09-06	15-09-06	19/09/06	25-09-06	26/09/06
Hours of Filtration	338	387	477	620	650
Sample #	63363	63462	63525	63907	63984
Varnish Potential Index	98	89	91	92	97
Gravimetric Patch wt mg/100ml	7	3	4	5	4
FTIR Oxidation absorbance units	5.64	5.66	5.7	5.61	5.58
Particle Count # of particles >4µ	248	248	421	496	382
Ruler % Remaining additive	83.9	82.7	82.7	78.4	81.1
RPVOT					
Sequence #	16	17	18	19	20
Date of Sample	27/09/06	3/10/2006	6/10/2006	24/10/06	2/11/2006
Hours of Filtration	674	815	890	1321	1490
Sample #	64074	64337	64555	65186	65706
Varnish Potential Index	94	100	94	82	86
Gravimetric Patch wt mg/100ml	4	3	4	4	4
FTIR Oxidation absorbance units	5.64	5.51	5.47	5.01	5.1
Particle Count # of particles >4µ	287	478	793	200	362
Ruler % Remaining additive	79.1	79.0	71.1	89.1	81.4
RPVOT		174			

Table 1. Test Data Steam Turbine Oil Analysis Program

turbine for DCA upgrading. There was insufficient manpower at the plant to take care of an oil change, so prior purification of the oil was to be utilized, to see if an extension of the oil life could be achieved, which was successful. Samples were taken prior to installation of the ISO-Pur HR to establish a baseline reading and the last baseline sample is reflected as -624 hours of filtration, and the first in the sampling sequence. A sample was taken after just one hour of

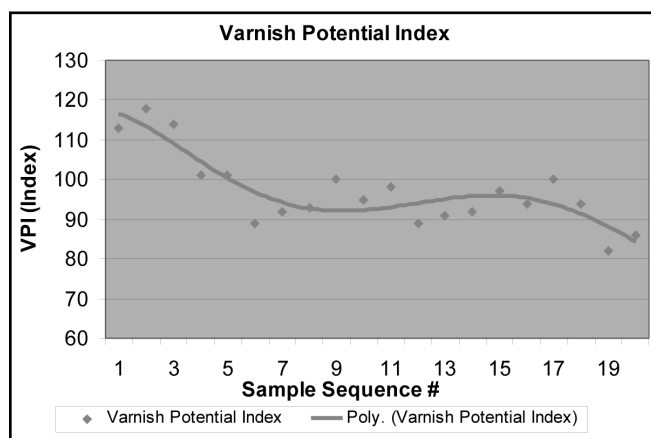


Figure 1. Varnish Potential Index for Steam Turbine Oil Samples

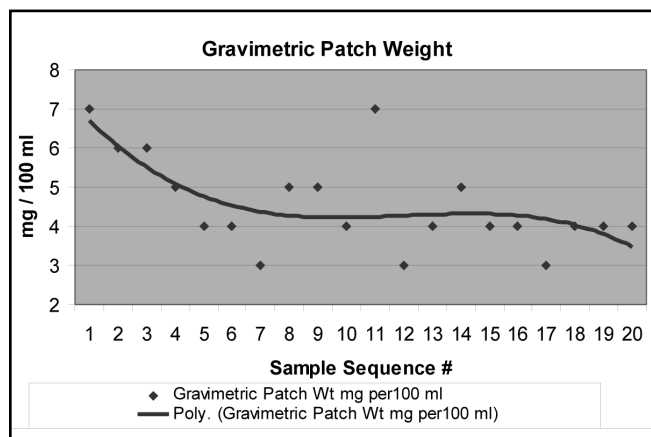


Figure 2. Gravimetric test data for Steam Turbine Oil Samples

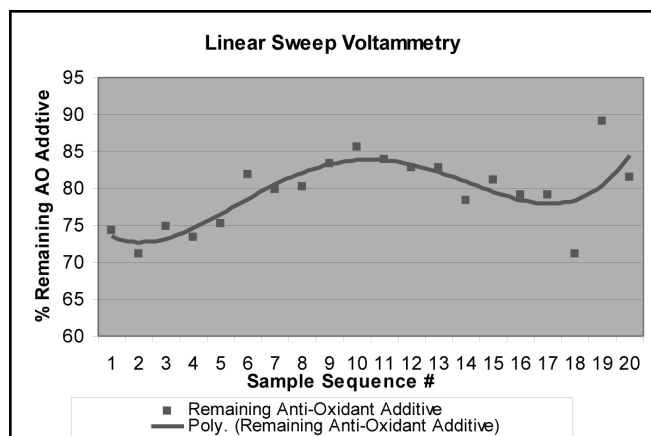


Figure 3. Remaining Antioxidant Additive for Steam Turbine Oil Samples

filtration for a total of 20 samples, reflecting a total of 1490 hours of filtration, at a filtration flow rate of 74 liters per minute. The data and charts are provided below.

From the data and figures above it is clear that VPI correlated well with the other tests, as the cleanliness of the oil improved due to purification by the BCA technology. The VPI and RULER® correlated well. What was found to be interesting is the improvement in RULER® and RPVOT values. It is thought that the lower levels of impurities in the oil allow the RULER® and RPVOT tests to be measured more significantly.

Sequence #	1	2	3	4	5
Date of Sample	Nov 1 2006	Dec 6 2006	Dec 7 2006	Dec 8 2006	Dec 12 2006
Hours of Filtration	-144	2	23	45	143
Sample #	65782	67379	67442	67517	67631
Varnish Potential Index	74	62	45	53	52
Gravimetric Patch wt mg/100ml	11	8	9	7	8
FTIR Oxidation absorbance units	5.46	5.44	5.53	5.46	5.44
Particle Count # of particles >4µ	1051	612	229	258	717
Ruler % Remaining additive	56.2	67.5	65.7	69.7	65.9
Oil Temp @ the ISOPur	78.5	75.3	74.2	75.4	76.1
Sequence #	6	7	8	9	10
Date of Sample	Dec 13 2006	Dec 14 2006	Dec 15 2006	Dec 18 2006	Dec 21 2006
Hours of Filtration	168	192	211	288	360
Sample #	67705	67773	67798	67946	68204
Varnish Potential Index	55	50	59	55	53
Gravimetric Patch wt mg/100ml	10	9	9	9	9
FTIR Oxidation absorbance units	5.46	5.45	5.42	5.34	5.32
Particle Count # of particles >4µ	277	1038	378	863	788
Ruler % Remaining additive	62.3	68.7	69.1	65.5	65.9
Oil Temp @ the ISOPur	76.5	75.5	73.1	72.9	73.1
Sequence #	11	12			
Date of Sample	Jan 08 2007	Jan 15 2007			
Hours of Filtration	793	934			
Sample #	68862	69147			
Varnish Potential Index	59	58			
Gravimetric Patch wt mg/100ml	6	5			
FTIR Oxidation absorbance units	5.47	5.46			
Particle Count # of particles >4µ	354	315			
Ruler % Remaining additive	73.7	72.3			
Oil Temp @ the ISOPur	73.2	73.2			

Table 2. Gas Turbine oil analytical data for oil samples between November 01 and Jan 15

Gas Turbine Results

The gas turbine was a GE Frame VI with a lubricating oil reservoir holding 6,700 liters of ISO VG 32 oil. The lube oil had accumulated approximately 61,500 running hours prior to the ISO-Pur BCA, Model HR Series, being installed. The ISO-Pur BCA Technology was tried on the gas turbine, due to the successful trial on the steam turbine, and in part, due to previous problems experienced by a sister power plant using this same oil type. It was thought that by purifying the oil, there may be the possibility to avoid the decision making process of changing brands or type of oil. This has been the successful outcome, with the decision being made to continue using this brand of oil in this turbine, despite the oil-related failures at the sister power plant. Samples were taken prior to installation of the ISO-Pur HR to establish a baseline reading and the last baseline sample is reflected as -144 hours of filtration, and the first sample in the sampling sequence. A sample was taken after just 2 hours of filtration for a total of 12 samples, reflecting a total of 934 hours of filtration, at a filtration flow rate of 74 liters per minute. The data and charts are provided below.

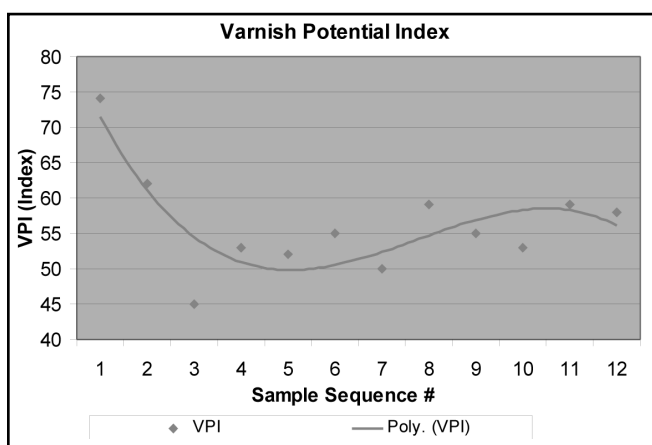


Figure 4. Varnish Potential Index Test Data for Gas Turbine Oils

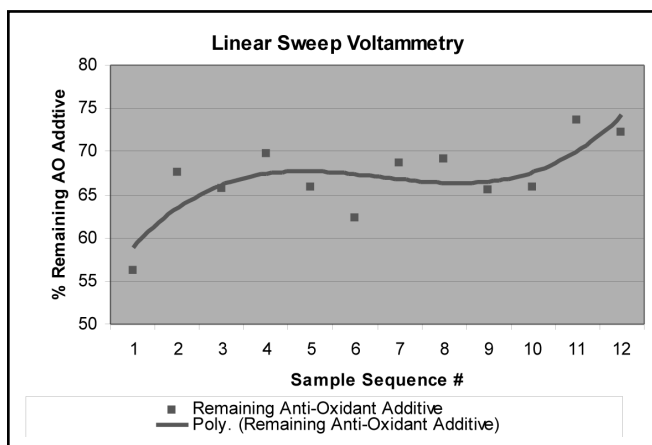


Figure 5. RULER Remaining Antioxidant Additive for Steam Turbine Oil Samples

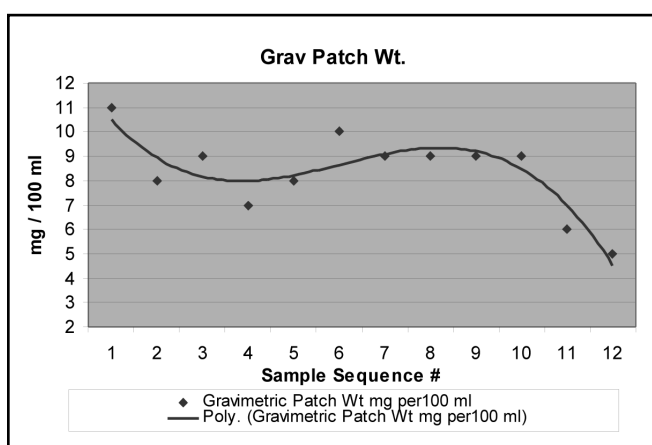


Figure 6. Gravimetric Patch Test Data for Gas Turbine Oils

From the data and figures above, we can conclude again, that the VPI correlated well with the other tests as the cleanliness of the oil improved due to purification by the BCA technology. Also of interesting note, was the reduction in oil temperature, as measured at the filtration unit. The turbine operator has been experiencing high

lube oil temperatures and was not well equipped to try and service the lube oil cooler, which was thought to be coated with varnish. This reduction in oil temperature has convinced the turbine operator to utilize the BCA technology on their second gas turbine as well, to help with high lube oil temperatures on that unit.

Summary

- VPI test is found to respond well and work well in both directions, in degrading oil quality and improving oil quality situations, as correlated with other conventional oil quality and oil cleanliness test methods.
- Linear Sweep Voltammetry (RULER method) shows a marked correlation with not only oil quality, as measured by percent remaining AO additive, but also with cleanliness levels. Furthermore, LSV can be used to supplant RPVOT in those high-value RPVOT oils that tend to have accuracy and repeatability problems.
- BCA technology is capable of successfully cleaning oil and improving the oil's measured life, thus reducing unnecessary oil changes due to poor accuracy of the oil testing methods caused by oil impurities.

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